



Fabricating Graphite Coated Copper Via Airbrushing

S. Ghorbanian, C. Zamani*, and H. Ahmadi Dermeni

School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, Tehran, Iran.

Received: 1 November 2021; Accepted: 1 June 2022

*Corresponding author email: c.zamani@ut.ac.ir

ABSTRACT

Airbrushing is a simple, cost-effective, and easy-to-use method for applying thin layer coatings. In this study, the fabrication of a graphite layer using airbrush spraying has been investigated, which requires stable graphite suspensions without any noticeable sedimentation before and while spraying. Aqueous suspensions with different ratios of Polyvinylpyrrolidone (PVP) to graphite were prepared. PVP was used as a surfactant that can disperse graphite particles in water, which also binds graphite particles to the substrate. For testing each suspension's stability, the turbidity of all samples was measured. The test demonstrated a specific ratio of PVP to graphite that makes the suspension most stable, which is 0.3g. A lower or higher amount of PVP was seen to make the stability worse. The sample with 0.3 grams PVP had the lowest sedimentation rate and thus was chosen for spraying. This optimum composition was sprayed on the substrate using an airbrush, and a graphite coat was obtained in the next step. The main application for the graphite-coated thin layer is in Li-ion batteries as a graphite-based anode.

Keywords: Graphite, Coating, Airbrush, Suspension, Turbidity

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronic products. However, there are still some concerns for their applications in electric vehicles and renewable energy storage grids, including energy density, cost, and safety [1]. Beck and Ruetschi highlighted the “Three E” criteria, namely, energy (high-energy content to unit weight and volume), economics (low manufacturing costs), and environment (safe, non-toxic), to determine the suitable energy storage system that meets the needs of application [2]. The high energy capacity, longer lifetime, and the light weight make the Li-ion battery the most potent power storage compared to other secondary batteries such as lead-acid, nickel-cadmium, and nickel-metal hydride batteries [2]. Lithium-ion batteries are made large-scale by the tape casting method, which is a relatively expensive process and requires a lot

of energy and time. In this research, an attempt has been made to investigate an alternative method for making electrodes for lithium-ion batteries. Graphite has been applied to a broad range of industries due to its high electrical and thermal conductivity, low coefficients of thermal expansion, self-lubrication, high oxidation resistance, and low wettability by liquid metals [3]. At present, graphite is the mainstay negative electrode material for commercial LIBs, which can theoretically provide a maximum specific capacity of 372 mAh.g^{-1} [4]. Recently, unconventional battery designs have worked towards developing battery technologies that can be used in devices and applications without constraining their form factors. Some examples are thin and flexible batteries, stretchable textile energy storage, paper batteries, micro-batteries, and transparent batteries [5]. Printing (or generally, painting) is already considered a viable technique

for large-area fabrication of electronic devices (circuits, photovoltaics, displays, etc.) on virtually any type of substrate [5]. Using an airbrush to spray the contents of a graphite anode on a current collector is a less expensive and faster method than conventional electrode fabrication methods. The general view of this method is that the active material of the anode (graphite) is mixed with a binder and then spread in a fluidized medium to form a suspension. This suspension should have low viscosity to be adequately sprayed. Then this suspension is sprayed on a current collector using an airbrush to form a thin layer of graphite coating. Graphite cannot be dispersed in water due to its hydrophobic surface. The use of dispersant/surfactant would provide an opportunity to enhance the graphite dispersion, decrease the coating viscosity, and improve the conductivity of surface-coated paper [6]. By adding a suitable surfactant, graphite particles are more stable in water. Although the larger graphite particles will settle to the bottom, a more stable suspension of graphite remains in the middle region of the sample, which contains smaller graphite particles. This stable part can be extracted and used for spraying.

In LIBs, a polymeric binder is essential in forming an electrode by binding active materials and ensuring their adherence to metallic current collectors such as copper or aluminum. Fig. 1 shows three possible binding mechanisms of a polymeric binder in electrodes. The first schematic illustrates the point binding mechanism, showing the uniform distribution of the binder and an excellent electronic conduction network. Spraying the mixture of active materials and binder can improve dispersion of binder in the coated layer. As depicted in Figs. 1(b) and (c), the second and third mechanisms are not desirable due to the poor electronic conduction by

localized connections between the active materials and the electrical conducting agents and due to an insulating polymer film which forms on the current collector [7].

The first Li-ion batteries marketed by Sony utilized petroleum coke at the negative electrode. Coke-based materials offer good capacity, 180 mAh/g, and are stable in the presence of propylene carbonate (PC)-based electrolytes, in contrast to graphitic materials [8]. In the mid-1990s, most Li-ion cells utilized electrodes employing graphitic spheres, particularly a Mesocarbon Microbead (MCMB) carbon. MCMB carbon offers higher specific capacity, 300 mAh/g, and low surface area, thus providing low irreversible capacity and good safety properties. Recently, more comprehensive carbon types have been used in negative electrodes. Some cells utilize natural graphite, available at a meager cost, while others use hard carbons that offer capacities higher than possible with graphitic materials [8].

In order to fabricate the Li-ion battery's electrodes, a homogenous mixture of constituent materials is needed. One of the most favorable solvents in anode slurry is water. However, graphite is not stable in a water-based medium, causing sedimentation of graphite particles. This will result in inconsistency of suspension's concentration over time and the electrodes will vary in performance. This study aims to prepare stable aqueous suspension for room-temperature coating of the electrode material on the current collector. Yakimchuk et al. fabricated a graphene suspension used in inkjet printing. The suspension consisted of graphene, water as a basic medium, ethanol as an optimizer of the printed layer drying process, and ethylene glycol which prevents the coffee-ring effect to occur [9]. In this study, however, the suspension comes in three components: graphite,

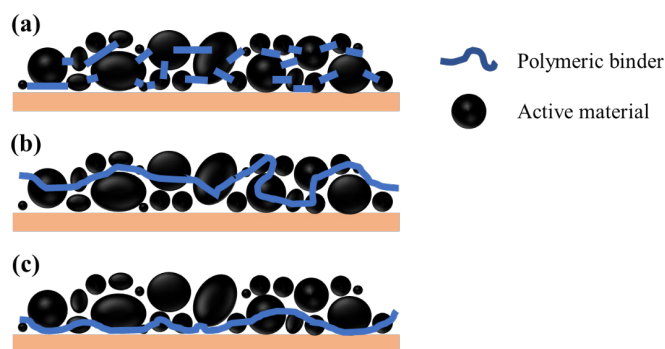


Fig. 1- Schematic of different binding mechanisms on the electrode surface. a) Point-binding mechanism, b) No binding between active material and the substrate, and c) No inter-particle binding.

water, and PVP as binder, which at the same time acts as a surfactant via dispersing graphite particles in the aqueous substance. Mancillas-Salas et al. investigated the effect of temperature on the ζ -potential of different samples of graphene oxide [10] and showed that the ζ -potential increased with temperature, especially as temperature goes from 20 to 30 °C (which coincides with the process conditions used in this work). Increased ζ -potential leads to a more stable suspension.

2. Experimental details

Five aqueous suspensions (25ml in volume) were prepared according to Table 1. First, PVP was dissolved in water. In the next step, graphite was added on a weight percent basis. All five samples were stirred on a magnetic stirrer for 15 minutes, sonicated for 1 hour, and immediately prepared for turbidity testing. A turbidity test was performed on each sample for 8 hours (with the exception of sample S1-0.5 which was tested for 5 hours), with 15 minutes between each test. The purpose of this

test was to detect a suspension with maximum stability within the longest period of time among all samples. The most stable sample will be used for the second stage of the experiment and would be sprayed on the substrate surface.

For measuring the stability of suspensions, an in-house made turbidity test equipment was employed, of which, the schematic structure is provided in Fig. 2a. The device is comprised of a laser light source (2W, wavelength of 532 nm) embedded in a completely dark chamber with a standard-size sample holder inside. A photocell is also fixed to the other side of the box, which enables the operator to collect light signals transmitted through the colloidal samples. The amount of light passing through each suspension was measured using the photocell via transforming the light intensity into the electrical resistance (in k Ω). The whole assembly is presented in Fig. 2b. As time passes and the graphite particles settle into the bottom of samples and their concentration decreases, more light passes through each sample, and the photocell shows a smaller amount of resistance accordingly. Then the results were normalized for comparison. The digital images of the sedimentation behavior of the sample S1-0.3 compared to the sample S0.5-0.5 are shown in Fig. 3 where sedimentation is observed clearly.

Molecular changes were investigated using a Fourier-transformed Infrared (FTIR) spectrometer

Table 1- Suspensions' composition tested in this study

Sample Code	Graphite (g)	PVP (g)
S1-0.1	1	0.1
S1-0.2	1	0.2
S1-0.3	1	0.3
S1-0.5	1	0.5
S0.5-0.5	0.5	0.5

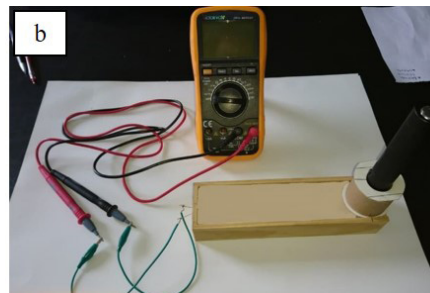
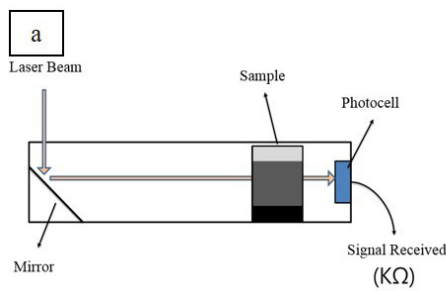


Fig. 2- Turbidity test device: a) schematic of the device showing the relative position of the mirror, sample, and the photocell, b) digital image of the setup.

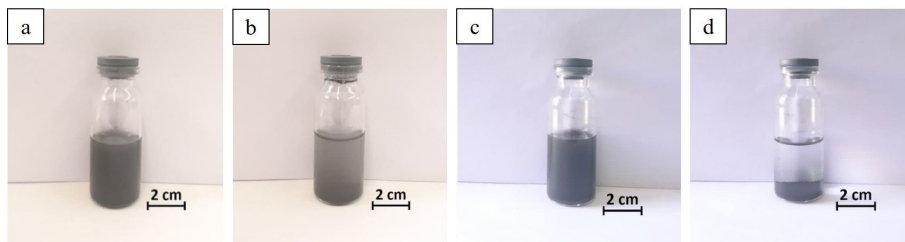


Fig. 3- Sedimentation behavior: a) as-prepared sample S1-0.3, b) sample S1-0.3 after 8 hours, c) as-prepared sample S0.5-0.5, d) sample S0.5-0.5 after 8 hours.

(PerkinElmer Spectrum 400) in the range of 450 cm^{-1} to 4000 cm^{-1} . An airbrush with a nozzle size of 300 μm was used to spray the most stable sample and form a graphite coating. The surface of the substrates was ground with P1500 sandpaper. The substrate was heated up to 100 $^{\circ}\text{C}$ on a hot plate. The airbrush used a 20psi air compressor, and the spraying was done with a distance of 20cm to the substrate. Airbrush was moved horizontally throughout the process to achieve a uniform coating.

3. Results and discussion

The turbidity test results for samples are shown in Fig. 4 where plots of turbidity vs. storage time are provided. Detailed investigation of these curves show that the majority of samples reveal major turbidity loss down to 30% or less within 8 hours of storage. Table 2 summarizes these results. Based on the obtained values presented in this table, the sample containing 0.3 gr PVP (denoted with S1-0.3) offers the best stability compared to other samples, keeping its turbidity to an acceptable level (about 53% of the original value) during 8 hours of storage. Also, in the case of this sample, the second stage of sedimentation process takes 6 hours. On the other hand, the sample with an equal amount of graphite and PVP (denoted with S0.5-0.5) loses about 78% of its initial stability after 3 hours, thus presenting the fastest turbidity drop among all

samples. Nevertheless, the sample presents about 5 hours of stability in the second stage, meaning that it can be the second option following the S1-0.3 sample. Taking other samples into consideration, the S1-0.1 and S1-05 with about 2.5 hours of stability reveal the shortest stability times.

In all samples, a three-stage curve is observed so that each colloid experiences a sharp drop in a short time due to the decrease of concentration in the middle of the sample's height. This is to the large tendency of these particles to settle and form the sediment at the bottom. Then, they enter a plateau (rather stable) region for a while. In the final stage, another sharp drop is seen again. In all suspensions, and over time, the heaviest and coarsest graphite particles naturally settle and form the primary sediment layer (first stage). Gradually, smaller particles begin to recede and enter the lower region from the upper area of the sample, which can justify the relative stability of the concentration in the middle of the experiment (second stage). Finally, after a specific time, the graphite particles in the upper region gradually settle which is accompanied by a decrease in concentration (third stage). All in all, and considering the designed coating procedure, 8 hours of stability would be a suitable time span for conducting coating process.

In this work, PVP is considered as the coupling agent that creates a bond between water molecules and graphite particles. In this case, it can be argued

Table 2- Turbidity values for tested samples

	S1-0.1	S1-0.2	S1-0.3	S1-0.5	S0.5-0.5
Min. Turbidity (%)	15.62	29.60	52.98	53.86*	21.67
Turbidity Drop (%)	84.38	70.40	47.02	46.14*	78.33
2 nd Stage Start (hrs)	3.5	1	0.5	0.5	3
2 nd Stage End (hrs)	5.75	4.5	6.5**	3.0	8
Duration of Stability Period (hrs)	2.25	3.5	6	2.5	5

* Data taken after 5 hours

** Continued to 8 hours

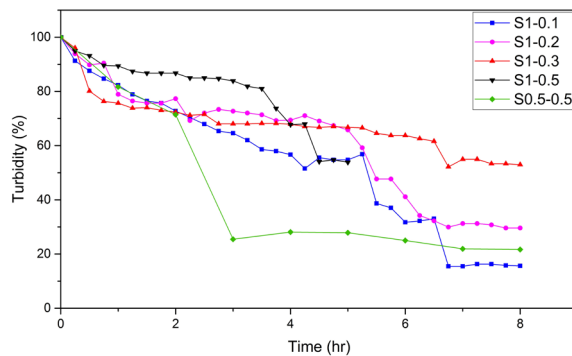


Fig. 4- Turbidity test results (%), showing the best stability in S1-0.3 sample over 8 hours of time.

that by changing the ratio of graphite and PVP, the share of each graphite particle in PVP molecules is affected.

If the amount of PVP in the sample is lower than a critical value, the share of each graphite particle in creating intermolecular bonds with the binder is considerably lower which means that most graphite particles do not undergo physical interactions and remain intact. Therefore, it leads to more and more graphite sedimentation and less stability of the colloidal sample, as shown in Fig. 3. However, it offers an optimum amount of PVP, which causes the sample to keep its stability for a longer period of time. If the stability of the mixture is required for 8 hours or more, then the optimum amount of PVP is approximately between 30 percent and 50 percent of the graphite particles in the sample.

In order to study the efficacy of PVP binder in attaching to graphite particles, FT-IR spectra of PVP, graphite, and S1-0.3 samples were obtained. Results are disclosed in Fig. 5 where sharp and peaks resulting from molecular vibrations are observed. The strong (s) peak at 3435 cm^{-1} corresponds

to O-H stretching vibration of adsorbed water. Moving towards lower wave numbers, the weak (w) peak at 2924 cm^{-1} is related to C-H stretching vibration. The next peak (medium, m) at 1440 cm^{-1} is related to CH₂ bending vibration of PVP. Also, the strong (s) peak at 1664 cm^{-1} in PVP spectrum belongs to C=O stretching vibration, while the 1635 cm^{-1} peak of graphite (strong, s) is due to the stretching vibration of the C=C bonds on the surface of graphite. Finally, the C-N vibration peak (strong, s) appears at 1260 cm^{-1} [12]. This peak has appeared in the S1-0.3 sample, which indicated the attachment of PVP molecules to graphite particles. The effective attachment of PVP to graphite confirmed in FTIR studies reveals the improvement of graphite stability in the aqueous medium [10].

Considering above findings, sample S1-0.3 was selected for spraying under the mentioned conditions. The outcome of the spraying process is shown in Fig. 6 in which a thin uniform layer is deposited on copper surface successfully.

Figure 7 indicates that the flaky graphite particles are layered on top of each other via PVP,

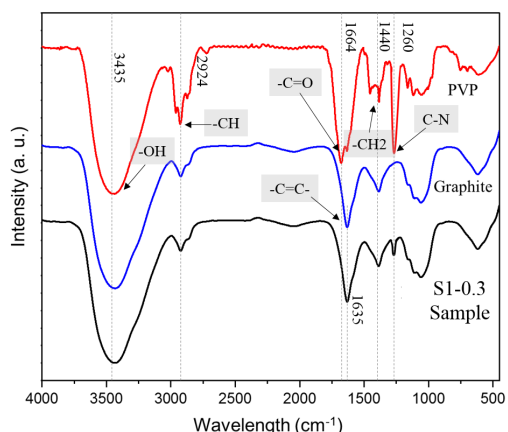


Fig. 5- FT-IR spectra of PVP, graphite and S1-0.3 sample confirming successful attachment of PVP to graphite.

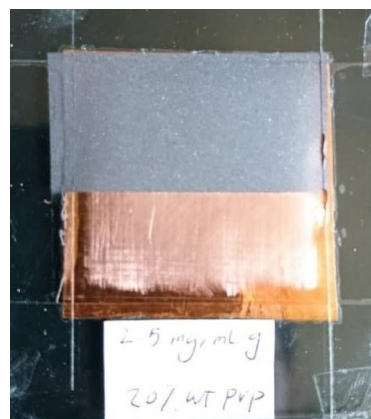


Fig. 6- Digital image of the graphite-coated thin layer of copper resulting from the spraying process. Formation of a uniform and flawless layer is clearly observable.

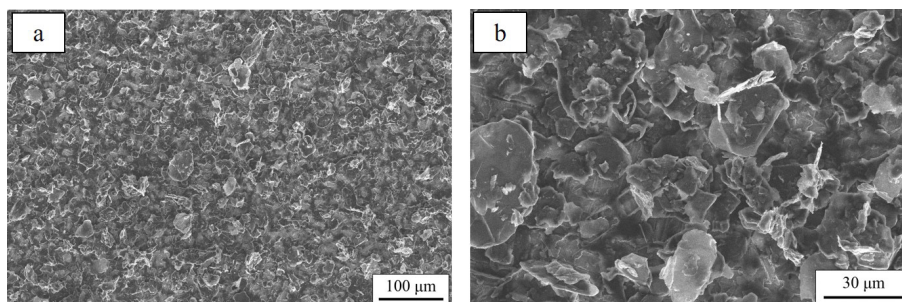


Fig. 7- FESEM micrograph of electrode surface: a) 600X, b) 2500X.

which acts as a binder at this point, fabricating a graphite layer with a high surface area.

4. Conclusions

In this study, the stability of graphite in an aqueous medium was enhanced by using PVP as a surfactant which has carbon-nitrogen bonds. The optimum ratio of PVP to graphite was 0.3,

resulting in the best graphite stability in water which starts after 30 minutes and lasts for six hours with 50% of initial turbidity. This composition was successfully used to fabricate a graphite coating on copper foils via airbrush. Results show that PVP acts as binder as well as a surfactant agent; thus dispersing graphite particles in the medium uniformly.

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